DRAFT
LAB ROUND TABLE FOCUS GROUP RECOMMENDATION
ANALYTICAL METHODS USED FOR CHEMISTRY ANALYSIS
RECOMMENDATION #1

15 May 2006

OBJECTIVE FOR *THE REQUIREMENT FOR UTILIZING USEPA APPROVED METHODS FOR LABORATORY ANALYSES*: To ensure that the monitoring results received for the Irrigated Lands Conditional Waiver Program are of reliable data quality for which the method capabilities, limitations and interferences are known. To ensure that analytical measurements are made using approved methodology.

PROBLEM STATEMENT: There is a need for flexibility when chemical analysis is required for constituents that have not received an EPA approval are needed for ILP monitoring (one example would be pyrethroids in sediment). The Analytical Requirements section of the draft Coalition Group MRP, Attachment B, Quality Assurance Project Plan (Section 4.1 Page 5) requires that laboratories used published methods to perform the analysis of the constituents list in Table 1 (Minimum Analytical Monitoring Requirements) of the draft Coalition Group MRP. Specifically, the draft MRP indicates that "Analytical methods used for chemistry analyses must follow a published method and document the procedure for sample analyses in a laboratory standard operation procedure (SOP) for review and approval."

Although laboratories analyzing samples for the Irrigated Lands Conditional Waiver Program are required to use published methods, adjustments may be required in order to analyze using the best method practical for the analyte of interest and to quantify at levels determined to be most-useful for the program. A current example would be the challenge for laboratories to maximize performance of existing analytical methods to perform the analysis of pyrethroids in sediment. The formal process to gain USEPA approval of an analytical method takes three years or greater. The protocol for development and validation of performance-based measurements (PBMs) is described by SWAMP (Surface Water Ambient Monitoring Program) and by NELAP (National Environmental Laboratory Accreditation Program), both of which have been derived from USEPA guidelines. The laboratory must provide the validation data and laboratory SOP upon request. Method reviewers, following the SWAMP or NELAP protocol for PBMs, will be able to audit the data package provided by the laboratory to ensure that method alterations have maximized method performance. Availability upon request of validation processes and SOPs will ensure transparency and discourage use of "secret" methods which may indeed work in one lab but which may not be reproducible by another laboratory. Flexibility within published methodology will be provided to laboratories. The regulated community will be assured that robust, repeatable, and validated analytical methods are in use for data generation.

RECOMMENDATION:

It is recommended that the narrative in the draft MRP, Attachment B QAPP Section 4.1 be changed to read: "Analytical methods used for chemistry analyses must follow a procedure approved by USEPA or provided in Standard Methods for the Examination of Water and Waste Water 19th Edition. Laboratories accredited for the use of United States Geological Survey (USGS), *American Society of Testing Materials* (*ASTM), and Association of Official Analitical Chemists (AOAC) methods may use these methods. In the event that ~~data quality objectives required~~ requirements ~~for~~ of the Conditional Waiver ~~compliance~~ cannot be supported by any of the above methods, then laboratories must submit a performance-based procedure for Central Valley Water Board staff approval. This will require a peer-reviewed published method (National Environmental Laboratory Accreditation Program NELAP) or performance-based validation method based upon the protocol described (SWAMP). Laboratory development of a validation package and Standard Operating Procedures (SOP) is required when analytes or quantification levels are outside the analyte list or differ by ten times the measurement levels stated in the published method. The validation package shall include all the elements for the "Initial Demonstration of Laboratory Capability", which contains:*

(1) Method Detection Limits (MDL) Studies (the analyst shall determine the MDL for each analyte according to the procedure in 40 California Federal Registration (CFR) 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method).

(2) Initial precision and recovery (IPR).

(3) Linear calibration ranges.

(4) Quality control sample (QCS), where applicable:

The laboratory must provide validation data and SOP upon request by the Central Valley Water Board staff. The SOPs requested for Performance Based Methods (PBMs) from laboratories will be kept confidential(1) among Central Valley Regional Board staff."

(1) Please read the "Regional Board Follow Items" (attach file for the recommendation #1) for more detailed on procedures to submitting confidential information to Central Valley Water Board.

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LAB ROUND TABLE FOCUS GROUP RECOMMENDATION
QUALITY CONTROL REQUIREMENTS FOR PHYSICAL PARAMETERS
RECOMMENDATION #2.1

15 May 2006

OBJECTIVE FOR *QUALITY CONTROL REQUIREMENTS FOR "PHYSICAL PARAMETERS*: Details of the procedures for field and laboratory quality control (QC) are an important technical procedure designed to ensure the integrity of analyses by proper operation and maintenance of equipment and instruments. Therefore, ILP requires these components as part of the QAPP to ensure that the data received from the coalitions has the highest quality through consistency in sample collection procedures and laboratory analysis.

PROBLEM STATEMENT: The Quality Requirements section of the draft Coalition Group MRP, Attachment B, Quality Assurance Project Plan (Section 5, Pages 7 and 8) requires field and laboratory control for all constituents listed in the Minimum Analytical Monitoring Requirement, Table 1 of the Draft MRP (page 9). For conventional chemical tests such as Organic, Metals, and Wet Chemistry methods, these QC requirements are currently being met. However, there are a number of tests for "Physical Parameters" that are not applicable to the conventional QC support data outlined in Table 1. Color, Turbidity, and Settleable/Suspended Matter are probably the most common. Due to the nature of the physical parameters being measured, "spike recovery data" are QC points, which do not apply. The components in a sample, which contribute to color, turbidity, or non-soluble materials, are unknowns. They are not identified; they are simply compared to a reference mark. Since the analyst does not know what these contributors are you cannot perform a matrix fortification.

RECOMMENDATION:
It is recommended that a narrative in the draft MRP Section 5.0 is included to read: "Quality Control requirements are expected to be applicable to all the constituents listed in Table 1 of the MRP, with exception of Color, Turbidity, and Settleable/Suspended, for which matrix spike, matrix spike duplicate, laboratory control spikes, laboratory control spikes duplicates, and surrogates are not required given the nature of analysis."

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LAB ROUND TABLE FOCUS GROUP RECOMMENDATION
QUALITY CONTROL FOR TABLE 1 ANALYTES
(FIELD DUPLICATES)
RECOMMENDATION #2.2

15 May 2006

OBJECTIVE FOR ***FIELD DUPLICATE AS ONE QUALITY CONTROL MEASURE*:** Field duplicates are an important indicator of good quality field sampling protocol. The field duplicates are an indicator of consistency in sample collection procedures that will ensure accurate and reproducible results.

PROBLEM STATEMENT:

The Field Quality Control section of the draft Coalition Group MRP, Attachment B, Quality Assurance Project Plan (Section 5.4. Pages 7-8) requires that laboratories have to reanalyze the field sample and its duplicate if the RPD is greater than 25%. Specifically, the draft MRP states, "If the RPD of field duplicate results is greater than 25% and the absolute difference is greater than the RL, both samples should be reanalyzed." The necessity for this recommendation is to allow for flexibility in the relative percent difference of 25% (RPD) for constituents that tend to have a greater variability due to the nature of the analytical method.

The purpose for collecting and analyzing field duplicates is to obtain an estimate of the variability in analytical results for a specific parameter, sample location, and time. There are three main sources of variation in the analysis of environmental samples; variation of the natural environment itself, variation in the sample collection and sub-sampling technique, and laboratory-based variation. The natural environment is highly variable and often is the largest source of variation even when samples are collected simultaneously. Field sampling and sub-sampling variation can be minimized by the use of good sampling techniques but they have no control over the natural variation. Laboratory variation increases as the analytical result approaches the method detection limit and varies by analytical method with some methods being less variable than others. Moreover, data obtained from multiple laboratories will also have increased variation due to differences in methods used and/or variation caused by sub-sampling techniques. Laboratories do minimize variation using good laboratory practices but the laboratory has no control over field sampling variation or natural variation.

QAPP requirements often include acceptance criteria placed on the laboratory based on field duplicate samples. These criteria are difficult for laboratories to achieve because of their lack of control over sampling and natural variation. Field duplicates are often replaced or enhanced by laboratory-based duplicates (i.e. sub-samples taken from the same sample bottle), but sub-sampling for laboratory duplicates is still dependant on the homogeneity of the sample. Therefore, laboratories will also analyze duplicate matrix

spikes, blank spikes, laboratory control materials, or certified reference materials in order to provide an estimate of the laboratory-based variation independent of the environmental samples.

Additional problems related to requiring laboratories to achieve acceptance criteria for field duplicates are short sample holding times that do allow enough time for the laboratory to do the re-analysis, e.g. microbiology samples, and results that at or near the MDL or PQL.

RECOMMENDATION:
It is recommended that the definition of a field duplicate be inserted into the draft MRP Section 5.4.

Field Duplicates *- A field duplicate sample will be collected at the rate of 5% field duplicates for each analysis (or one set per sampling event whichever is more frequent). Field duplicate sample will be collected in the same manner and as close in time as possible to the original sample or is an aliquot from a large-volume, fully mixed sample collected at a specified date/time and split into discrete sub-samples. This effort is to attempt to examine field homogeneity as well as sample handling, within the limits and constraints of the situation. Results from field duplicate analyses are for informational purposes to indicate natural variation or problems related field sampling techniques. Therefore, no QA/QC acceptance criteria are placed on the laboratory for precision with respect to field duplicates.*

It is also recommended that QAPP acceptance criteria for laboratory precision be based on laboratory-based duplicate samples only such as duplicate matrix spikes, blank spikes, laboratory control materials, or certified reference materials.-When the analysis of bacteria (E. coli or fecal coliform) is required, the laboratory must ensure that they have validated laboratory precision, and continue to meet quality control requirements as specified in Standard Methods 9020B, 19th Edition. Possession of valid CA ELAP or NELAP certification for microbiology of wastewater will satisfy requirements for analyses of bacteria (E. coli or fecal coliform).

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LAB ROUND TABLE FOCUS GROUP RECOMMENDATION
LABORATORY QUALITY CONTROL (METHOD BLANKS)
RECOMMENDATION #3

15 May 2006

OBJECTIVE FOR ***METHOD BLANK AS LABORATORY QUALITY CONTROL***: The necessity for this requirement is to ensure that analytical results are accurate measures of concentrations found in the field samples, and are not compromised by contamination from containers, reagents, preparation procedures, or instrumentation used during laboratory analysis.

PROBLEM STATEMENT: The objective of this recommendation is to allow for flexibility when analytes are present in the method blanks, if these analytes are inherent to a particular analytical method. The Laboratory Quality Control section of the draft Coalition Group MRP, Attachment B, Quality Assurance Project Plan (Section 5.5. Page 8) requires that laboratories have to re-analyze or re-extract the blank and associated samples for any analyte detected in the blank. Specifically, the draft MRP states "If any analyte is detected in the blank, the blank and the associated samples must be re-extracted and re-analyzed."

Analyses of certain constituents (i.e. metals by Method 6010A and Method 6020) measure low-level and trace amounts. This means the method is highly susceptible to blank contamination. The preparation of samples using certain analytical methods (i.e. Method 6010A and Method 6020 for metals such as copper, zinc, lead, arsenic, etc.) required the addition of acid as part of the extraction procedure. The analysis of organic constituents may also be susceptible to blank contamination for certain compounds such as Phthalates from sample containers or reagents and solvents from the laboratory environment. This can add "noise", which can also be described as fluctuations in the electronic signal from the instrument's detector**.** These fluctuations or background noise, in effect, determine the sensitivity of the instrument, because the only reliable signal then is one that is above the background "noise". This "noise" in the calibration blank could result in detection of the analyte in the method blank in cases where low-level measurements are being attempted.

Making the laboratories re-extract and re-analyze each time that there is an analyte detected in the method blank might not be the most effective solution and may be difficult to achieve by the laboratories that are working indirectly with Irrigated Lands Conditional Waiver Program through contracts with coalition groups. In some cases, re-extraction may not be possible due to limited sample volume available to the laboratory. Therefore, the Lab Round Table Focus Group is making the following recommendation to the TIC:

RECOMMENDATION:
When laboratories obtain detectable concentrations of a specific analyte in the method blanks as part of their laboratory quality control, they need to re-extract and re-analyze in the following circumstances:
"METALS: If any analyte concentration in the method blank is above the PQL, the lowest concentration of that analyte in the associated samples must be 10 times the method blank concentration. Otherwise, all samples associated with that method blank with the analyte's concentration less than 10 times the method blank concentration and above the PQL must be re-digested and re-analyzed for that analyte. The sample concentration is not to be corrected for the method blank value;
ORGANICS: If any analyte concentration in the method blank is above the PQL. all samples associated with that method blank must be re-extracted and re-analyzed for that analyte. The exception to the above requirement is for common laboratory contaminants such as volatile solvents and phthalates where all samples associated with that method blank with an analyte concentration less than 10 times the method blank concentration and above the PQL must be re-digested and re-analyzed for that analyte.

This approach will provide flexibility for the laboratories that are doing the analysis for the Coalitions through various contracts. It is expected that the proposed approach will be applied only to those constituents that are analyzed with methods that require specific preparation methods for extraction.

If the recommendation is implemented, the quality of the data provided will not be affected. Samples with detections close to the detection in the blank will still be re-analyzed.

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LAB ROUND TABLE FOCUS GROUP RECOMMENDATIONS
CHANGES TO THE MINIMUM MONITORING REQUIREMENTS (Table 1)

RECOMMENDATION #4.1. Addition of *FENPROPATHRIN*

The recommendation is to add Fenpropathrin to the pyrethroids analysis in water and sediment.

PROBLEM STATEMENT: Although Fenpropathrin is extensively used in agriculture throughout the Central Valley; the current Table 1 does not include it. The addition of this analysis to the list will provide the Central Valley Regional Board with information to be able to assess better toxicity results.

In addition, most laboratories surveyed indicated that they are already doing the pyrethroids analysis for the rest of the constituents in this group and the addition of fenpropathin will not be problematic.

RECOMMENDATION:
Add fenpropathrin to the pyrethroids analysis in water with a maximum PQL of 0.05 ug/L for water and 1ng/g for sediment.

RECOMMENDATION #4.2. Addition of *TOC IN SEDIMENT*

PROBLEM STATEMENT: Currently the analysis of TOC in sediment is not required. However, the LabRoundTable agreed that there is the need for requiring an additional Organic Carbon (OC) analysis for sediments since the low content of OC in the sediment may increase the bioavailability of hydrophobic toxicants to the organisms. Considerations of toxic levels of pyrethroids do need to include TOC.

RECOMMENDATION:
Include Total Organic Carbon analysis in sediment as part of the Minimum Analytical Monitoring Requirements. The analytical methods recommended for this analysis are EPA 415.1 and EPA 9060. The maximum PQL for this analysis is 200 mg/kg.